Chinese Journal of Catalysis 37 (2016) 1600–1607

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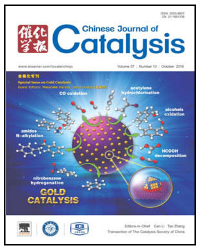

Review (Special Issue on Gold Catalysis)

Vinyl chloride monomer production catalysed by gold: A review

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ARTICLE INFO

Article history:
Received 22 April 2016
Accepted 6 June 2016
Published 5 October 2016

Keywords:
Gold
Acetylene
Hydrochlorination
Vinyl chloride monomer
Poly vinyl chloride
Catalysis

ABSTRACT

In this review we discuss the history of research into the use of gold for the acetylene hydrochlorination reaction, and describe the recent developments which have led to its commercialisation. We discuss the use of different precursors and the addition to gold of a secondary metal as methods which attempt to improve these catalysts, and consider the nature of the active gold species. The vast majority of poly vinyl chloride (PVC) produced globally still uses a mercuric chloride as a catalyst, despite the environmental problems associated with it. Due to the agreement by the Chinese government to remove mercury usage in the PVC industry over the course of the next few years there is an obvious need to find a replacement catalyst; the potential use of gold for this process has been well known for several decades and to date gold seems to be the best candidate for this, primarily due to its superior selectivity when compared to other metals.

1. Introduction

Vinyl chloride monomer (VCM) is the monomer from which poly vinyl chloride (PVC) is made. PVC is one of the most commonly used plastics and has a wide range of applications, for example in packaging, construction materials, medical devices and clothing. This is largely due to the ability to modify the properties of the substance using additives, for example to alter its rigidity. As a result, there is a high demand for the plastic, with over 40 million tonnes of PVC produced every year, leading to VCM being a very valuable chemical. The vast majority of VCM (around 90%) is used in the manufacture of PVC, with its alternative use being in the manufacture of chlorinated solvents.

There are a number of routes by which VCM may be produced industrially, depending on the starting material used. The most commonly used process in countries where oil is readily available is known as the balanced process; it is a combination of chlorination and oxychlorination reactions using ethene, which is oil-derived, as the starting material. Another, simpler method is the direct hydrochlorination of acetylene, which is a coal-derived starting material, and this reaction is traditionally catalysed by carbon-supported mercuric chloride. This latter route is how VCM was historically produced, and is now commonly used in China due to the availability of inexpensive coal, with over 13 million tonnes per year of VCM manufactured this way. However, the deactivation of the mercury-based catalysts is a significant problem and in addition to the decrease in activity, leaching of the mercury from the catalyst can be problematic due to its toxic nature. The resultant environmental issues with using mercury and the continued use of this process indicate the need for a new catalyst. In fact, the Minamata convention regarding mercury usage includes a clause which states that new VCM plants will not be allowed to use a mercury catalyst after 2017 and all VCM plants must be mercury-free after 2022. This has led to a resurgence in research in this field due to the necessity for a new, mercury-free catalyst. Gold is an excellent candidate for such a catalyst; in

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DOI: 10.1016/S1872-2067(16)62482-8 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 37, No. 10, October 2016

this review we discuss the history of research into its use for the acetylene hydrochlorination reaction, and describe the recent developments which have led to its commercialisation and the continuing research in this field.

2. The beginnings of gold catalysis

While supported metal catalysts have been used in industrial processes for a number of decades, the potential use of gold in such catalysts is a more recent development. At around a similar time, in the 1980s, two key discoveries were made which led to the now vast amounts of research being carried out into gold catalysts for a wide range of applications. Hutchings predicted and subsequently confirmed that based on electrode potentials, gold should be the most active metal for the hydrochlorination of acetylene, catalysed by carbon-supported metal chloride catalysts [1,2]. Meanwhile Haruta *et al.* [3] demonstrated that gold nanoparticles supported on transition metal oxides, *e.g.* Fe_2O_3, are active for the catalytic oxidation of CO at low temperatures. Previously, gold had largely been considered unreactive, although the use of gold catalysts had been reported for oxidations of ethylene and propylene [4] and reductions of olefins [5]. However, these new findings illustrated the potential use of gold as a catalyst when present in nanoparticle form. Since then, research into gold catalysis has increased virtually exponentially, leading to the publication of the first book on this subject in 2006 [6].

Despite their use even to the present day, deactivation of mercury-based catalysts has long been a problem; this was being investigated in some detail in the mid-1980s [7–9]. Prior to this, a study by Shinoda [10] investigated the activity of a wide range of carbon supported metal chloride catalysts for acetylene hydrochlorination and correlated the activity with the electron affinity of the metal cation, divided by the metal valence. The correlation consisted of two straight lines and is shown in Fig. 1; it can be seen that mercury has one of the highest activities of any of the metals considered. This correlation was used as a starting point for identification of potential improved catalysts for this reaction; subsequently, considering that the reaction is most likely a two-electron process, whereas electron affinity concerns a one-electron process, a study by Hutchings instead correlated the activity of supported metal chloride catalysts with their standard electrode potential [1] and obtained a curve, shown in Fig. 2. Based on this curve it was suggested that since its standard electrode potential has a greater value than those metals investigated, gold should be the most active metal for this reaction; this was later confirmed [2,11] and is illustrated in Fig. 3.

This correlation was further developed by Conte *et al.* [13]

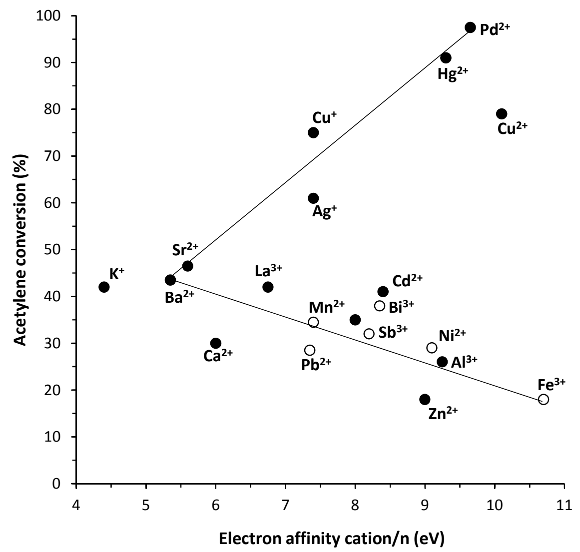

Fig. 1. Correlation of activity for acetylene hydrochlorination with electron affinity/metal valence for a range of carbon supported metal chlorides, replotted based on the data in Ref. [12].

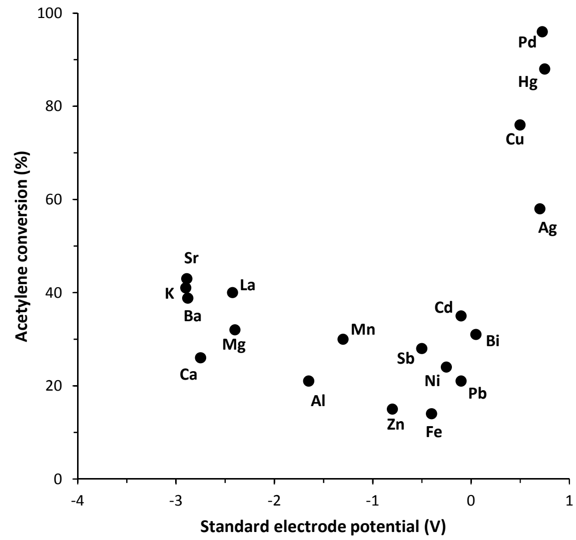

Fig. 2. Correlation of activity for acetylene hydrochlorination of carbon supported metal chloride catalysts with the standard electrode potential of the metal, $M^{n+} + ne^- \rightarrow M$, replotted based on the data in Ref. [12].

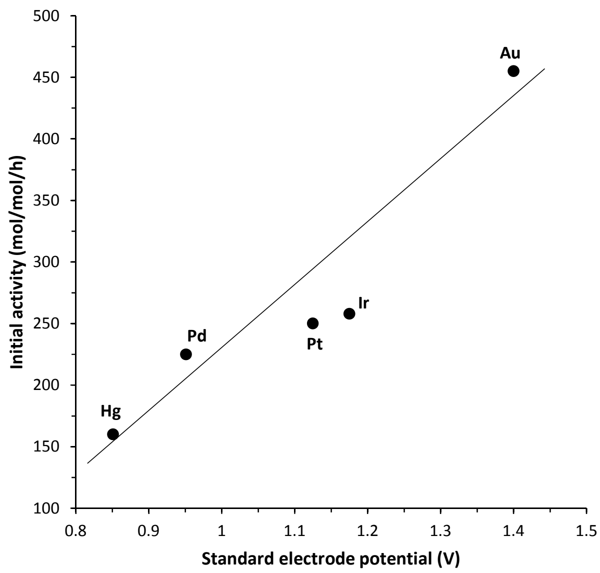

Fig. 3. Correlation of initial acetylene hydrochlorination activity with standard electrode potential for supported metal chlorides including Au replotted based on the data in Ref. [12].